

**PATENT**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

**Applicants:** Hidemitsu Aoki, et al.

**Examiner:** S. T. Chaudhry

**Serial No.:** unassigned

**Art Unit:** 1746

**Filed:** herewith

**Docket:** 12688A

**For:** METHOD FOR CLEANING  
SEMICONDUCTOR WAFER AFTER  
CHEMICAL MECHANICAL POLISHING  
COPPER WIRING

**Dated:** February 13, 2002

Assistant Commissioner for Patents  
Washington, D.C. 20231

**PRELIMINARY AMENDMENT**

Applicants submit the following Amendment for entry in the above-identified application.

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**CERTIFICATE OF MAILING BY EXPRESS MAIL**

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**Date of Deposit:** February 13, 2002

I hereby certify that this correspondence is being deposited with the United States Postal Service Express Mail Post Office to Addressee service under 37 C.F.R. § 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231.

**Dated:** February 13, 2002

  
Michelle Mustafa

### **IN THE SPECIFICATION:**

Please amend the specification as follows:

After the TITLE please insert the following:

### **--CROSS REFERENCE TO RELATED APPLICATION:**

The present application is a divisional of copending application Serial Number 09/313,027 filed on May 17, 1999.--

### **IN THE CLAIMS**

Prior to examination please cancel claims 1-24 without prejudice.

Please add claims 25-50 as follows:

--25. A method for cleaning a semiconductor wafer having a copper layer exposed to a surface thereof after a chemical mechanical polishing, comprising the steps of:

a) treating said semiconductor wafer with a first washer selected from the group consisting of aqueous ammonia containing ammonia at 0.0001 – 0.5 weight percent and a catholyte between neutral and weak base for removing polishing particles from said semiconductor wafer without damage to said copper layer; and

b) treating said semiconductor wafer with a second washer containing at least one decontaminating agent selected from the group consisting of polycarboxylic acids each capable of producing a chelate compound together with copper, ammonium salts of said polycarboxylic acids and polyaminocarboxylic acids for removing metallic contaminants from said semiconductor wafer.

26. A method for cleaning a semiconductor wafer having a copper layer exposed to a surface thereof after a chemical mechanical polishing, comprising the steps of:

a) treating said semiconductor wafer with a first washer selected from the group consisting of aqueous ammonia containing ammonia at 0.0001 – 0.5 weight percent, a catholyte between neutral and weak base and hydrogen containing water for removing polishing particles from said semiconductor wafer without damage to said copper layer; and

b) treating said semiconductor wafer with a second washer containing at least one decontaminating agent selected from the group consisting of polyaminocarboxylic acids for removing metallic contaminants from said semiconductor wafer.

27. The method as set forth in claim 25 or claim 26, in which a polishing slurry is used during said chemical mechanical polishing, and contains said polishing particles and at least one oxidizing agent serving as a contamination source for at least one of said metallic contaminants.

28. The method as set forth in claim 27 in which said polishing particles are brushed away from said semiconductor wafer, and said first washer allows said polishing particles and said surface to be negatively charged.

29. The method as set forth in claim 25 or 26, in which said catholyte is produced through an electrolysis in one of pure water and aqueous ammonia containing ammonia equal to

or less than 0.5 weight percent.

30. The method as set forth in claim 29, in which said catholyte contains said ammonia at 0.0005 – 0.01 weight percent.

31. The method as set forth in claim 26 in which said hydrogen-containing water is produced through a hydrogen bubbling in one of pure water and aqueous ammonia containing ammonia equal to or less than 0.5 weight percent.

32. The method as set forth in claim 31, in which said hydrogen-containing water contains hydrogen at 0.1 - 10 ppm.

33. The method as set forth in claim 32 in which said hydrogen-containing water further contains said ammonia at 0.0005 – 0.01 weight percent.

34. The method as set forth in claim 25, in which said polycarboxylic acids are oxalic acid, citric acid, D-tartaric acid, L-tartaric acid, malonic acid, malic acid malein acid or succinic acid.

35. The method as set forth in claim 25 in which said ammonium salts are salts of oxalic acid, citric acid, D-tartric acid, L-tartaric acid, malinic acid, malic acid, malein acid or succinic acid.

36. The method as set forth in claim 26, in which said catholyte and said hydrogen-containing water has an oxidation-reduction potential between -1000 milli-volt and -300 milli-volt when a reference electrode is formed of silver chloride.

37. The method as set forth in claim 25, in which said catholyte has an oxidation-reduction potential between -1000 milli-volt and -300 milli-volt when a reference electrode is formed of silver chloride.

38. The method as set forth in claim 28, in which said surface is formed of an insulating material selected from the group consisting of silicon oxide, benzocyclobutene, parrylene-N, cytop, xerogel, hydrogen silisesquiioxane and methylsilane based composite material containing hydrogen peroxide.

39. The method as set forth in claim 25 or 26 in which said second washer is supplied to a major surface of said semiconductor wafer where said copper layer is exposed, and a third washer containing hydrofluoric acid and hydrogen peroxide is supplied to a reverse surface of said semiconductor wafer.

40. The method as set forth in claim 39, in which said hydrofluoric acid, said hydrogen peroxide and water are regulated to 1-10 : 1-10 :200.

41. The method as set forth in claim 25 or 26, in which a centrifugal spray cleaning technique is used in said step b).

42. A method for cleaning a semiconductor wafer having a tungsten layer exposed to a surface thereof after a chemical mechanical polishing, comprising the steps of:

a) treating said semiconductor wafer with a first washer selected from the group consisting of aqueous ammonia containing ammonia at 0.0001 – 5 weight percent and a catholyte between neutral and weak base for removing polishing particles from said semiconductor wafer without damage to said tungsten layer; and

b) treating said semiconductor wafer with a second washer containing at least one decontaminating agent selected from the group consisting of oxalic acid, ammonium oxalate and polyaminocarboxylic acids and ranging from 0.01 weight percent to 7 weight percent for removing metallic contaminants from said semiconductor wafer.

43. A method for cleaning a semiconductor wafer having a tungsten layer exposed to a surface thereof after a chemical mechanical polishing, comprising the steps of:

a) treating said semiconductor wafer with a first washer selected from the group consisting of aqueous ammonia containing ammonia at 0.0001 – 5 weight percent, a catholyte between neutral and weak base and hydrogen containing water for removing polishing particles from said semiconductor wafer without damage to said tungsten layer; and

b) treating said semiconductor wafer with a second washer containing at least one decontaminating agent selected from the group consisting of polyaminocarboxylic acids and ranging from 0.01 weight percent to 7 weight percent for removing metallic contaminants from said semiconductor wafer.

44. The method as set forth in claim 42 or 43, in which a polishing slurry is used during said chemical mechanical polishing, and contains said polishing particles and at least one oxidizing agent serving as a contamination source for at least one of said metallic contaminants.

45. The method as set forth in claim 44, in which said polishing particles are brushed away from said semiconductor wafer, and said first washer allows said polishing particles and said surface to be negatively charged.

46. The method as set forth in claim 42 or 43 in which said catholyte is produced through an electrolysis in one of pure water and aqueous ammonia containing ammonia equal to or less than 5 weight percent.

47. The method as set forth in claim 43, in which said hydrogen-containing water is produced through a hydrogen bubbling in one of pure water and aqueous ammonia containing ammonia equal to or less than 5 weight percent.

48. The method as set forth in claim 45, in which said surface is formed of an insulating material selected from the group consisting of silicon oxide, benzocyclobutene, parrylene-N, cytop, xerogel, hydrogen silisesquioxane and methylsilane based composite material containing hydrogen peroxide.

49. The method as set forth in claim 42 or 43, in which said second washer is supplied to a major surface of said semiconductor wafer where said tungsten layer is exposed, and a third washer containing hydrofluoric acid and hydrogen peroxide is supplied to a reverse surface of said semiconductor wafer.

50. The method as set forth in claim 49, which said hydrofluoric acid, said hydrogen peroxide and water are regulated to 1 – 10 : 1- 10: 200.

51. The method as set forth in claim 42 or 43, in which a centrifugal spray cleaning technique is used in said step b).--

#### **REMARKS**

The present application is a divisional application of copending U.S. Patent application Serial No. 09/313,027, ("027 application"), filed on May 17, 1999.



The '027 application is directed, inter alia to a method for cleaning a semiconductor wafer having a copper layer exposed to a surface thereof after a chemical mechanical polishing, comprising the steps of:

a) treating said semiconductor wafer with a first washer selected from the group consisting of hydrogen containing water for removing polishing particles from said semiconductor wafer without damage to said copper layer; and

b) treating said semiconductor wafer with a second washer containing at least one decontaminating agent selected from the group consisting of polycarboxylic acids each capable of producing a chelate compound together with copper, ammonium salts of said polycarboxylic acids for removing metallic contaminants from said semiconductor wafer.

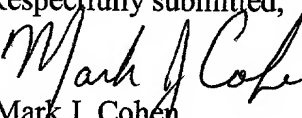
During prosecution thereof, a restriction requirement was imposed in which applicant was requested to elect between the various species in the first washer and the various species of the second washer.

Pursuant to the restriction requirement, applicants elected the first washer to be hydrogen containing water and the second washer to be polycarboxylic acids. However, the U.S. Patent and Trademark Office also permitted the second washer to include copper and ammonium salts of the polycarboxylic acids. The remaining subject matter was not examined in the parent application. More specifically, the non-elected subject matter resulting from the imposition of the restriction requirement consisted of the remaining combination and permutations of the subject matter recited in claims 25 et. seq. In other words, the non-elected subject matter is directed to a method for cleaning a semiconductor wafer in which the semiconductor wafer is treated with a first washer and a second washer, wherein, in a first embodiment, the first washer

is selected from the group consisting of aqueous ammonia and a catholyte between neutral and weak base and the second washer is polycarboxylic acid each capable of producing a chelate compound together with copper, ammonium salts of said polycarboxylic acids and polyaminocarboxylic acids or wherein, in a second embodiment, the first washer is aqueous ammonia, the catholyte between neutral and weak base or hydrogen containing water and the second washer is polyaminocarboxylic acid. The present application is directed to the non-elected subject matter.

Wherefore, the present application is in condition for allowance.

Respectfully submitted,

  
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